



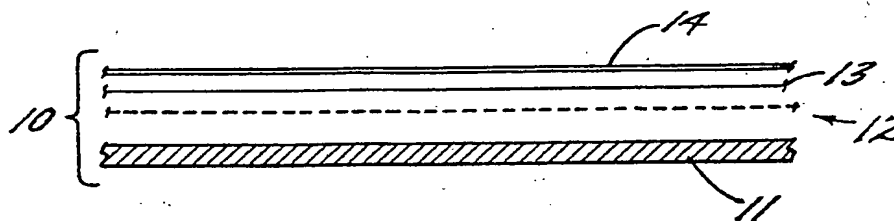
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<p>(21) International Application Number: PCT/US89/04088 (22) International Filing Date: 18 September 1989 (18.09.89) (30) Priority data: 246,674 19 September 1988 (19.09.88) US (60) Parent Application or Grant (63) Related by Continuation US 246,674 (CIP) Filed on 19 September 1988 (19.09.88) (71) Applicant (for all designated States except US): REXHAM CORPORATION [US/US]; 90 Park Avenue, New York, NY 10016 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): WINTON, Robert, A. [US/US]; 157 Watroak Drive, Pineville, NC 28134 (US). CHRISTIE, Eugene, F. [US/US]; 6721 Folger Drive, Charlotte, NC 28211 (US).</p>		<p>(74) Agents: LINKER, Raymond, O., Jr. et al.; Bell, Seltzer, Park & Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US. Published With international search report.</p>

(54) Title: IMPROVED FLUOROPOLYMER-METAL LAMINATES



(57) Abstract

The present invention provides articles with a bright metallic appearance that are lightweight, economical and have long life. These articles are formed of a protective, weather-resistant, transparent film (14) overlying a special surface-treated metal substrate (11). The surface treatment comprises an unusually thin chromate, phosphate or anodized treatment (12). The protective film (14) is a cast, molecularly unoriented fluoropolymer. An adhesive layer (13) is positioned between the protective film (14) and the metal substrate (11) and bonds the protective film (14) to the metal substrate (11). The adhesive layer (13) comprises an acrylic resin adhesive and optionally a zircoaluminate adhesion promoter.

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IMPROVED FLUOROPOLYMER-METAL LAMINATES

Field of the Invention

The present invention relates to metal articles, the surfaces of which are specially treated and subsequently protected from the degradative effects of the environment by a laminate comprising a fluoropolymer film. These metal articles have an improved bright metal surface appearance and greater formability.

Background of the Invention

Polished or plated metal has been used for many years to provide durable and decorative surfaces in a number of applications. For example, chrome has been used to provide such a bright decorative surface to designated parts such as car bumpers and trim. Chrome, however, is being designed out of current applications because of its weight, uncertain availability and expense.

In a number of applications, other bright polished metals such as aluminum can provide a similar appearance to chromium while avoiding the weight, expense and uncertain availability associated with chromium. Aluminum is abundantly available, relatively light in weight, durable, and forms a protective coating of aluminum oxide about 50 angstroms thick, which makes it highly resistant to ordinary corrosion.

Aluminum is, however, susceptible to attack by acids and bases, and polished aluminum surfaces do not resist weathering, but instead develop a milky

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appearance that generally results from the aluminum oxide coating. Because of aluminum's advantages in weight and durability, however, a number of techniques have been developed in attempting to protect aluminum, and these techniques have met with varying degrees of success.

One technique is chemical anodization which provides improved protection and the option of color tinting. Anodization, however, has not been demonstrated to result in long-term protection on exposed parts under many environmental conditions, and the use of the process itself is under increasing environmental pressure because of the problems associated with waste disposal requirements for the spent chemicals used in the surface anodization process. Anodization also tends to embrittle the aluminum, limiting the extent to which post-anodization forming techniques can be successfully used.

Another technique for protecting aluminum is the direct coating of the aluminum with a polymer. This generally provides some advantages over anodization in terms of protection. Typical polymer coating processes, however, require extensive solvent handling, followed by baking or curing of the polymer after its application. Furthermore, polymer coatings often either are or become brittle, delaminate, and show "orange peel," "cracking," "crazing," or "blushing" exterior effects after exposure. Clear vinyl coatings, which are sometimes used to face a bright metal, can also mold, mildew or stain.

Yet another technique is the lamination of a polymeric film to an aluminum surface using an adhesive. Laminates have similar advantages to polymer coatings, however, they often lack clarity, do not exhibit long-term bond durability, and exhibit poor formability. Formability means that the finished metal may be worked, whether by stamping, pulling, or

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bending, without affecting the decorative surface. One of the advantages of metals is their malleability, ductility, and flexibility. Accordingly, coatings or protective surfacing films which will not withstand such metal-working techniques are lacking in utility. Other shortcomings that a surface treatment should overcome include poor adhesion, and susceptibility to heat, water, solvent, mechanical scrubbing and biological attack.

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Summary of the Invention

The present invention provides metal articles having a metallic surface appearance which is protected against weathering, and which will withstand severe post-forming without discoloration or delamination. The articles comprise a metal substrate, a thin metal surface treatment coating on the surface of the metal substrate, and a protective weather resistant surfacing layer bonded to the thin metal surface treatment coating and formed of a cast, molecularly unoriented fluoropolymer film. Metal articles in accordance with the present invention will withstand weather exposure without cracking or blushing, will exhibit water clarity, and will maintain clarity and lamination upon severe post-forming. Severe post-forming refers to a process in which the article is stamped, bent or drawn, resulting in elongation of 7 percent or greater. Metal articles in accordance with the present invention are capable of withstanding post-forming that results in elongation of 20 percent or greater without cracking, crazing or delamination. The protective surfacing layer is suitable for tinting with pigments or dyes or both, and avoids development of an objectionable surface appearance after extended exposure to the environment.

35

A preferred embodiment of the present invention is a metal-polymer composite having a metallic surface appearance that is protected against weathering, and

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which will withstand severe post-forming without discoloration or delamination, said composite comprising a metal substrate, a thin metal surface treatment coating on the surface of said metal substrate, and a protective weather resistant surfacing layer bonded to said thin coating and formed of a cast, molecularly unoriented fluoropolymer film. More specifically, the metal-polymer composite may comprise a fluoropolymer film, an acrylic resin adhesive layer, and a metal substrate, wherein the surface of the metal substrate has been chromate treated, phosphate treated or anodized. The adhesive layer optionally contains a zircoaluminate adhesion promoter. Preferably, the fluoropolymer film comprises a polyvinylidene fluoride-containing polymer.

Brief Description of the Drawings

Figure 1 is a perspective view of an automobile, for which items according to the present invention can form useful decorative parts.

Figure 2 is a partial cross-sectional perspective view of an automobile body side molding taken along lines 2-2 of Figure 1.

Figure 3 is a partial cross-sectional perspective view of an automobile window trim strip taken along lines 3-3 of Figure 1. Figures 2 and 3 are post-formed pieces fabricated from an aluminum-fluoropolymer composite in accordance with the present invention.

Figure 4 is an exaggerated cross-sectional view of the piece of molding shown in Figure 3 illustrating the metal substrate 11, the metal surface treatment 12, the acrylic adhesive 13, and the protective weather resistant surfacing layer 14.

Detailed Description

A metal article whose surface has been rendered resistant to weathering in accordance with the present invention includes a metal substrate which may be in

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various forms, such as sheet, rod, bar, block or other form, and may be composed of various metals, such as aluminum, stainless steel, copper, or other metal. Depending upon the desired final appearance, the surface of the metal substrate may be polished or provided with a textured surface such as a brushed surface. In the embodiment illustrated, the metal article 10 is an automobile window trim strip. Figure 4 is a cross-sectional schematic of the article shown in Figure 3. The metal substrate 11 comprises a thin, ductile sheet of aluminum having a bright, polished surface.

Immediately overlying the metal substrate is a thin metal surface treatment 12. The metal surface treatment 12 is applied at a thickness significantly less than the conventional thickness for such treatment when the surface treatment is used alone as the protective coating for the metal surface. The specific thickness of the surface treatment will depend on the type of surface treatment. For example, in fabricating the composites of the present invention, a chromate metal surface treatment should desirably have a chromate layer of less than or equal to about 25 mg/ft². Typical chromate treatments useful for external applications call for approximately 75 mg/ft². A commercially available source of chromate for chromate conversion coating is Bonderite K-702. Another commercially available source of chromate is Parker AmChem's TD 1309 IN chrome phosphate treatment. Nonchrom containing phosphate surface treatments used in the present invention should have a treatment deposit of less than 90 mg/ft². Preferably, the phosphate treatment comprises between 30 to 90 mg/ft² phosphate. Typical phosphate treatments useful for external applications are approximately 500 mg/ft². A commercially available source of a phosphate coating is Parcolene 333 (iron phosphate). Finally, when the

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surface of a metal substrate is to be anodized in accordance with the present invention, a surface treatment of 0.08 mils or less, and preferably 0.04 mils or less is used. Normally, anodized surfaces useful in exterior applications will comprise a surface coating of approximately 0.6 mils, and may be as low as 0.2 mils. See generally, Metals & Plastics Publications, Inc., Metal Finishing Guidebook Directory, 1988, 451-495 (1988); ASM International, The Surface Treatment & Finishing of Aluminum and Its Alloys, (5th Ed. 1987); and Reynolds Metals Co., Finishes for Aluminum, (1967).

These thin surface treatments prove to be more economical by reducing the amount of expensive materials required, such as chromate. In addition, certain efficiencies result from the lighter weight products that are produced. Other advantages afforded by the thin metal surface treatments of the present invention include improved adhesion of the protective polymeric layer to the metal substrate. The thinner surface treatments of the present invention also result in reduced embrittlement and crazing. Consequently, the metal-polymer composites of the present invention have improved formability, i.e., they can undergo severe post-forming without discoloring or delaminating. By severe post-forming we mean elongation of the metal-fluoropolymer composite by 7 percent or greater.

In contrast, for example, metal-polymer composites fabricated from 5657 alloy aluminum anodized to standard thickness, e.g., for an Everbright® finish, and a fluoropolymer protective layer performed well in accelerated weathering tests, however, the anodized treatments crazed during part forming. A very thin anodized coating avoids the crazing problem, but has inadequate abrasion and corrosion resistance to be used alone. Similarly, other surface treatments when

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applied as a particularly thin coating, provide a treated metal substrate that can be severely post-formed without crazing, e.g., chromate coatings and phosphate coatings provide soft, bright, and formable treated metal substrates, however, these also have reduced abrasion and corrosion resistance.

The protective surfacing layer 14 which overlies the metal treatment 12 protects the composite from abrasion and corrosion. The protective surfacing layer should be a substantially molecularly unoriented cast film, as opposed to a film which has been oriented or biaxially oriented. Such films are prepared by a number of known liquid casting methods, such as by spreading a solvent solution having a polymer dissolved therein onto a carrier with a casting die, doctor bar, or reverse roll coater, then evaporating the solvent, and then stripping the polymer film from the carrier. The reverse-roll coating method is the preferred method of making liquid cast films for the present invention. Other liquid casting methods are also known and useful for practicing the present invention. In appropriate cases, a plastisol, organosol, or dispersion of the polymer can be cast onto the carrier instead of a solvent solution. For example, polytetrafluoroethylene, which is virtually insoluble, can be cast as a dispersion. Thus, for purposes of the present invention, "substantially molecularly unoriented cast films" are liquid cast films, and not melt cast films or films formed by extrusion.

Polymers suitable for forming the protective weather resistant surfacing layer will not significantly fade, peel, chalk, or crack, when exposed to the environment, for the intended life of the product. Such weatherable polymers include fluoropolymers and blends thereof with other compatible weatherable polymers such as acrylate polymers.

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Fluoropolymers useful for practicing the present invention include polymers and copolymers formed from trifluoroethylene, tetrafluoroethylene, hexafluoropropylene, monochlorotrifluoroethylene and dichlorodifluoroethylene. Copolymers of these monomers formed from fluoroolefins such as vinylidene fluoride are also useful. Further illustrative examples of fluoropolymers useful for practicing the present invention include polyvinyl fluoride, polyvinylidene fluoride, fluorinated ethylene/propylene copolymers ("FEP" resins), ethylene/chlorotrifluoroethylene copolymers, vinylidene fluoride/hexafluoropropene copolymers, and vinylidene fluoride/perfluoro (alkyl vinyl ether) dipolymers and terpolymers with tetrafluoroethylene. Illustrative of the commercially available fluoropolymers useful for practicing the present invention are those sold under such trademarks as KYNAR, FORAFLOX, SOLEF, VIDAR, LUMIFLOX AND FLUOREX. A preferred weatherable polymer for use in the present invention is a polymer alloy of polyvinylidene fluoride and one or more other polymers such as acrylic polymers. Acrylic polymers are thermoplastic polymers or copolymers of acrylic acid, methacrylic acid, esters of these acids, or acrylonitrile. Because one of the objects of the present invention is to provide and maintain a bright, metal surface appearance, acrylics are chosen for their clarity. A commercially available source of such a polymer alloy film is Rexham Corporation Industrial Film division's Fluorex A, an alloy of polyvinylidene fluoride polymer and methylmethacrylate.

Positioned between the treated metal substrate 11, 12 and the weather resistant protective layer 14 is an adhesive layer 13. The adhesive layer comprises an acrylic adhesive. A preferred example of a commercially available acrylic adhesive is methyl methacrylate copolymer (at 45% solids) in toluene

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supplied by Rohm & Haas (B48). Preferably, this is blended with monopropylene glycol monomethyl ether, e.g., Union Carbide's UCAR PM, in a ratio of about 2.5:1 weight solids.

5 Acrylic adhesives exhibit high clarity, similar to that of the acrylic polymers, but generally do not form an especially durable bond between materials as dissimilar as a metal and a fluoropolymer. That
10 shortcoming is circumvented by the adhesion promoting attributes of the thin metal surface treatments described herein.

 Alternatively, that shortcoming can be remedied by the addition of adhesion promoters. Adhesion
15 promoters are chemical additives that, when added to an adhesive in a small quantity (typically less than two percent based on resin solids), greatly increase the work required to separate the adhered materials.

 Zircoaluminate adhesion promoters are well suited to this purpose. Zircoaluminate organometallic
20 adhesion promoters are surface modifiers which are hydrolytically and thermally stable coordinate covalent complexes comprising aluminum and zirconium. The compositions are reactive with various metals and thereby enhance the adhesion of coatings to metals.
25 Zircoaluminates typically are formed of a zirconium building block, an aluminum building block, and an organic functional portion. In the present invention, preferred adhesion promoters include amino functional zircoaluminate compounds supplied in a propylene glycol
30 solvent, such as the promoter available from Cavedon Chemical Company, Inc. under the designation CAVCO MOD APG, and carboxy functional zircoaluminate compounds in propylene glycol-methyl ether solvent mixtures available from the same source under the designation
35 CAVCO MOD CPM.

 Therefore, when a strong bond between a weather resistant protective layer and an untreated metal is

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desired, the adhesive layer of the present invention will include an adhesion promoter in addition to the acrylic adhesive. Conversely, by surface treating the metal substrate in accordance with the present invention, the zircoaluminate adhesion promoters become optional.

The adhesive layer may also include one or more ultraviolet light stabilizers. These stabilizers are useful because nonpigmented polyvinylidene fluoride is transparent to ultraviolet light and the underlying metal is reflective to it. As a result, the adhesive and the optional adhesion promoter are both constantly exposed to both incident and reflected ultraviolet light in outdoor environmental applications. Light stabilizers prevent degradation of the adhesive or adhesion promoter by ultraviolet light by quenching the degradation reactions caused by ultraviolet light. As an example, benzophenone may be blended with a quenching type molecule such as a hindered amine to achieve stabilization.

The invention further comprises the method of forming a metal-polymer composite having a metallic surface appearance that is both weather-resistant and workable. More specifically, the present invention provides a method of fabricating a metal-polymer composite having a metal surface appearance that is protected against weathering, and which will withstand severe post-forming without discoloring or delaminating comprising applying a thin metal surface treatment to a metal substrate, overlaying the surface treated metal substrate with a protective weather resistant surfacing layer formed of a cast, molecularly unoriented fluoropolymer film, and bonding said surfacing layer to said surface treated metal substrate with an adhesive layer formed of an acrylic adhesive.

Where a laminate is desired, the method comprises laminating a protective vinylidene fluoride

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polymer film to the surface treated metal substrate using an adhesive layer comprising an acrylic resin adhesive, and which may optionally contain a zircoaluminate adhesion promoter.

5 In one embodiment, the method comprises applying the adhesive layer to the surface of the vinylidene fluoride polymer film following which the protective film is laminated to the treated surface of the metal substrate with the adhesive therebetween. In
10 such circumstances, the metal substrate may be heated when the protective film is laminated thereto. In a preferred embodiment, the protective film is applied to the metal substrate by nipping the film onto the substrate with a nipping roll.

15 In another embodiment, the method of the invention comprises applying the adhesive layer to the treated surface of the metal substrate, following which the protective vinylidene fluoride polymer film is laminated to the surface of the treated metal substrate
20 upon which the adhesive was applied. In this embodiment the protective film may be laminated to the metal substrate while the metal substrate is in a heated condition and may be applied by nipping the film onto the substrate with a nipping roll.

25 In yet another embodiment, the finished article can be produced by fabricating a primer coating comprised of a dilute solution of the acrylic resin material to the treated surface of a metal substrate, then applying an acrylic resin adhesive to the surface
30 of a film formed of a polymer which contains polyvinylidene fluoride, and then laminating the coated surface of the protective film to the primer-coated metal substrate. If desired, a small amount of the adhesion promoter may be added to the either the
35 acrylic resin material or the adhesive layer. As in the previous embodiments, the protective film may be laminated to the metal substrate while the metal

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substrate is in a heated condition and by using a nipping roll.

While laminating a film to a substrate is a convenient method of practicing the present invention, it is not the only method. Particularly preferred embodiments of the present invention rely on casting the adhesive layer and the polymeric protective layer onto the treated metal substrate. Such a method comprises, e.g., coating the acrylic adhesive layer onto the treated surface of the metal substrate, over which the resin containing the polyvinylidene fluoride and acrylic polymers is then cast to form the film.

More specifically, the metal-polymer composite may be produced by arranging a spray-line that applies a first back coating of the acrylic adhesive to the surface treated substrate, followed by a second back coating of fluoropolymer, followed by drying. Drying may be accomplished in stages or after both coats. We contemplate that by applying the adhesive layer and polymeric protective layer to a freshly treated metal substrate advantages of economy, superior adhesion, enhanced appearance, efficiency and time are achieved. Furthermore, we contemplate that by optimizing the peak metal temperature, e.g., as high as possible without degrading the acrylic adhesive, during fabrication of the composite, whether by lamination or casting, that the adhesion promoting attributes of the metal treatment are even further enhanced.

The following examples illustrate some of the preferred techniques, and the characteristics of the resulting products.

Example

Samples of Everbright Aluminum Quality 5657 aluminum alloy with H25 hardness, 0.025 inch thickness, and R5 Bright Dipped were used as the metal substrate. Three metal substrates were surface treated with the following thicknesses of a sulfuric acid anodized and

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sealed coating: 0.080 mils, 0.040 mils, 0.015 mils. A fourth such metal substrate was left untreated as a control (0.000 mils). To each of the substrates was applied a thermoplastic acrylic adhesive; and over that a polyvinylidene fluoropolymer weather resistant surfacing layer comprising FLUOREX. Each of the four substrates were then subjected to four tests intended to demonstrate the formability of the composites, the relative amount of adhesion, ability to retain a bright metal surface appearance and resistance to staining. The results and a brief description of each test is set forth below:

	Fluoropolymer Film	Anodized Thickness (Mils)			
		.080	.040	.015	0.000
15 Bending Radius (inches)	Yes	1.5	1.2	.6	<0.1
Edge Lifting (in ²)	Yes	.26	.49	.52	.72
Brightness (%R)	Yes	78	76	72	78
Brightness (%R)	No	77	74	65	52
Sulfide Staining	Yes	Pass			
20 Sulfide Staining	No	Fail			

DESCRIPTION:

Bending Radius: Determined by bending the composite into a uniform circular bend until visually apparent crazing occurs, at which point the radius is determined.

Edge Lifting: At edges of 3" x 6" sample after 2000 hours of Harshaw salt fog exposure at 100 degrees fahrenheit.

Brightness: Total reflectance measured by an ACS Spectro Sensor II after 2000 hours of Harshaw salt fog exposure at 100 degrees Fahrenheit.

Sulfide Staining: Measured according to General Motors' specification FBMS 26-7.

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The data demonstrates that thicker anodized coatings have greater adhesion and improved appearance. However, thinner anodized coatings have better formability. Regardless of the surface treatment thickness, anodized coatings are sensitive to chemical staining. Thus, a fluoropolymer film provides chemical resistance, brightness durability, and when overlaid on a thin anodized coating demonstrates improved adhesion durability.

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That Which Is Claimed Is:

1. A metal-polymer composite having a metallic surface appearance that is protected against weathering, and which will withstand severe post-forming without discoloration or delamination, said composite comprising:
 - a metal substrate;
 - a thin metal surface treatment coating on the surface of said metal substrate; and
 - a protective weather resistant surfacing layer bonded to said thin coating and formed of a cast, molecularly unoriented fluoropolymer.
2. A metal-polymer composite according to Claim 1 wherein said thin metal surface treatment coating is selected from the group consisting of a chromate coating of a thickness of about 25 mg/ft² or less, a phosphate coating of 90 mg/ft² or less, and an anodized coating of a thickness of 0.08 mils or less.
3. A metal-polymer composite according to Claim 1 including a transparent acrylic adhesive layer bonding said weather resistant surfacing layer to said thin surface treatment coating.
4. A metal-polymer composite according to Claim 3 wherein said transparent acrylic adhesive layer includes a zircoaluminate adhesion promoter.
5. A metal-polymer composite according to Claim 3 wherein said transparent acrylic adhesive layer includes an ultraviolet stabilizing component.
6. A metal-polymer composite according to Claim 1 wherein said fluoropolymer comprises a preformed film.

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7. A metal-polymer composite according to Claim 1 wherein said fluoropolymer comprises a coating.

8. A metal-polymer composite according to Claim 1 wherein said fluoropolymer is a vinylidene fluoride containing polymer.

9. A metal-polymer composite according to Claim 8 wherein said vinylidene fluoride containing polymer comprises a polyvinylidene fluoride and acrylic polymer alloy.

10. A metal-polymer composite according to Claim 1 wherein said metal substrate comprises an aluminum sheet, and wherein the article has been severely post-formed such that the aluminum sheet includes regions which have been elongated by 7 percent or greater without discoloration or delamination of said weatherable surfacing layer.

11. A metal-polymer composite having a metallic surface appearance that is protected against weathering, and which will withstand severe post-forming without discoloration or delamination, said composite comprising:

a metal substrate;

a thin metal surface treatment coating on the surface of said metal substrate, said coating being selected from the group consisting of a chromate coating of a thickness of about 25 mg/ft² or less, a phosphate coating of 90 mg/ft² or less; and an anodized coating of a thickness of .00008 inch or less;

a protective weather resistant surfacing layer overlying said thin coating and formed of a cast, molecularly unoriented transparent vinylidene fluoride containing polymer; and

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a transparent acrylic adhesive layer bonding said weather resistant surfacing layer to said thin coating.

12. A metal-polymer composite having a metallic surface appearance that is protected against weathering, and will withstand severe post-forming without discoloration or delamination, said composite comprising:

a metal substrate;

a protective weather resistant surfacing layer overlying the surface of said metal substrate and formed of a cast, molecularly unoriented fluoropolymer;

and

an adhesion promoting layer positioned between said protective surfacing layer and said metal substrate adhering said protective surfacing layer to said metal substrate, said adhesion promoting layer comprising an acrylic resin adhesive and a zirconium aluminate adhesion promoter.

13. A metal-polymer composite according to claim 12 wherein said fluoropolymer comprises a vinylidene fluoride containing polymer.

14. A metal-polymer composite according to claim 13 wherein said vinylidene fluoride containing polymer comprises a polyvinylidene fluoride and acrylic polymer alloy.

15. A method of fabricating a metal-polymer composite having a metal surface appearance that is protected against weathering, and which will withstand severe post-forming without discoloring or delaminating comprising:

applying a thin metal surface treatment to a metal substrate;

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overlaying the surface treated metal substrate
with a protective weather resistant surfacing layer
10 formed of a cast, molecularly unoriented fluoropolymer;
and

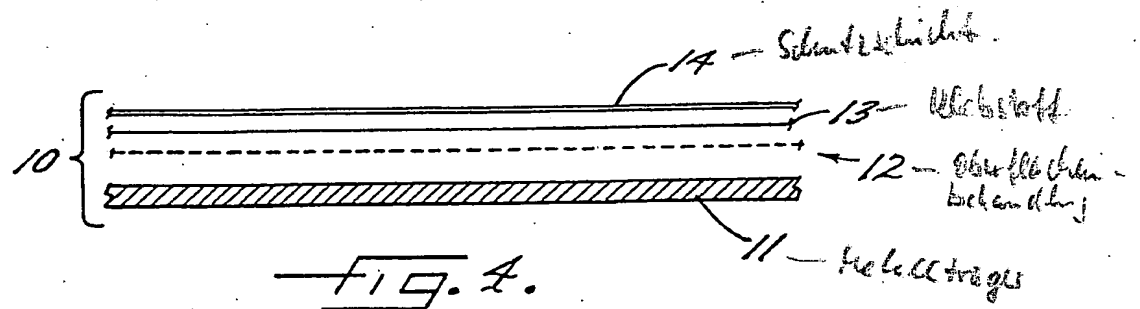
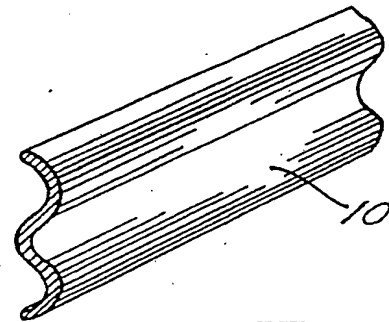
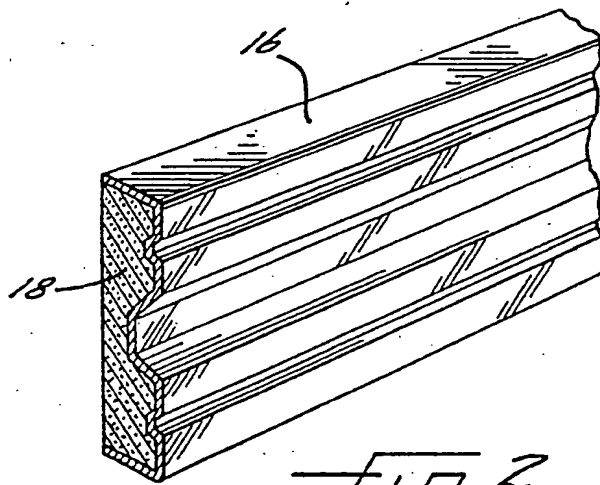
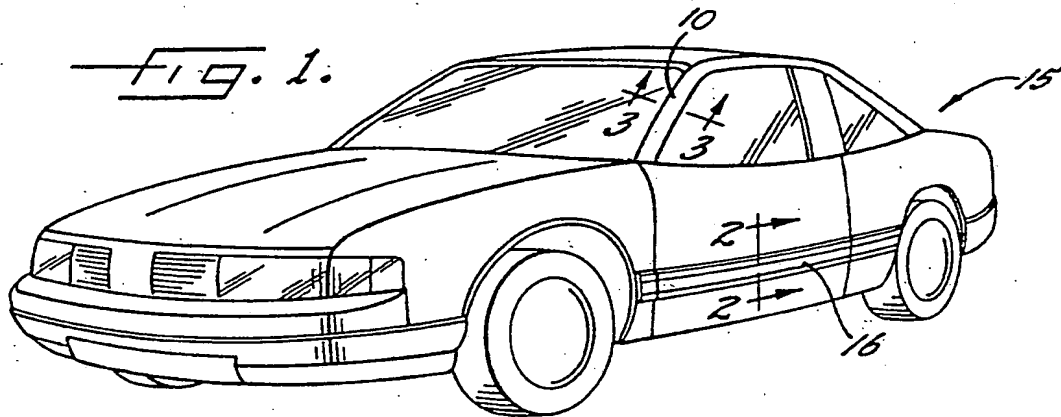
bonding said surfacing layer to said surface
treated metal substrate with an adhesive layer formed
of an acrylic adhesive.

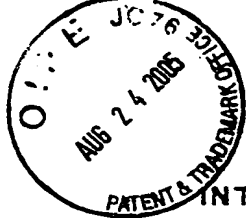
16. The method of claim 15 wherein the step of
applying a thin metal surface treatment comprises
applying a surface treatment selected from the group
consisting of a chromate coating of a thickness of
5 about 25 mg/ft² or less, a phosphate coating of 90
mg/ft² or less, and an anodized coating of a thickness
of 0.08 mils or less.

17. The method of claim 16 wherein the
fluoropolymer is a polyvinylidene fluoride containing
polymer.

18. A method of fabricating a metal-polymer
composite having a metal surface appearance that is
protected against weathering, and which will withstand
severe post-forming without discoloring or delaminating
5 comprising: overlaying a protective film formed of a
cast, molecularly unoriented fluoropolymer on the
surface of a metal substrate; and bonding said
surfacing layer to said substrate by positioning
therebetween an adhesive layer comprising an acrylic
10 adhesive and a zircoaluminate adhesion promoter.

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/04088

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(4) B32B 15/08; B60R 13/04; C23C22/78		
U.S. CL. 156/327, 333; 428/31, 421, 422, 463		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	156/237, 333; 428/31, 421, 422, 463	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 3,325,344 (SEMANCIK) 13 JUNE 1967	1-18
A	US, A, 3,526,532 (HEIBERGER) 1 SEPTEMBER 1970	1-18
A	US, A, 4,272,585 (STRASSEL) 9 JUNE 1981	1-18
A	US, A 4,317,861 (KIDOH) 2 MARCH 1982	1-18
A	US, A 4,444,826 (SASAKI) 24 APRIL 1984	1-18
A	US, A, 4,650,526 (CLAFFEY) 17 MARCH 1987	1-18
A, P	US, A, 4,810,540 (ELLISON) 7 MARCH 1989	1-18
<p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
07 NOVEMBER 1989		01 DEC 1989
International Searching Authority		Signature of Authorized Officer
ISA/US		HENRY F. EPSTEIN